

**Characterization Of Early Solar System Aqueous Fluids In Extraterrestrial Samples.** M. Zolensky<sup>1</sup>, R. Bodnar<sup>2</sup>, A. Dolocan<sup>3</sup>, J. Han<sup>4</sup>, R. Hanna<sup>5</sup>, I. Gearba<sup>3</sup>, Q.H.S. Chan<sup>6</sup>, T. Ireland<sup>7</sup>, C. Goodrich<sup>8</sup>, M. Matsumoto<sup>9</sup>, A. Tsuchiyama<sup>10</sup>, L. Le<sup>11</sup>; <sup>1</sup>ARES, NASA JSC, Houston TX 77058, USA (michael.e.zolensky@nasa.gov); <sup>2</sup>Dept. of Geosciences, Virginia Tech, Blacksburg VA 24061, USA; <sup>3</sup>Texas Materials Institute, Univ. of Texas, Austin, TX 78712, USA; <sup>4</sup>Univ. of Houston; Houston TX 77204, USA; <sup>5</sup>University of Texas High-Resolution X-ray Computed Tomography Facility (UTCT) Austin, TX 78712, USA; <sup>6</sup>Royal Holloway University, Egham Surrey, TW20 0EX, UK; <sup>7</sup>University of Queensland, Brisbane St Lucia, QLD 4072, Australia; <sup>8</sup>LPI-USRA, Houston, TX 77058, USA; <sup>9</sup>Tohoku Univ., Sendai 980-8578, Japan; <sup>10</sup>Ritsumeikan University, Kusatsu 525-8577, Japan; <sup>11</sup>Jacobs JETS, Houston, TX 77058 USA.

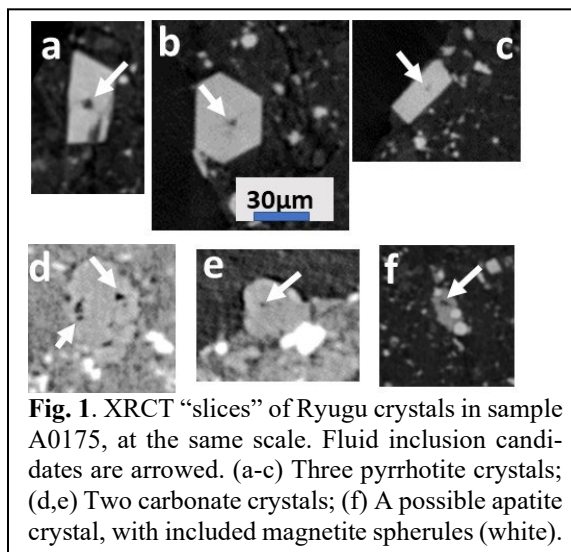
**Introduction:** Our primary objective is to make chemical and isotopic measurements of individual, pre-selected aqueous fluid inclusions in a wide range of secondary phases in the least terrestrially-altered astromaterials currently available - Ryugu samples collected by the Hayabusa2 Mission [1,2]. Our goal is to explore the compositions of the aqueous fluids that were active on the parent body of asteroid Ryugu early in its history.

**Locating Fluid Inclusions:** Preserved early solar system fluids are mostly likely to be found in astromaterials that have experienced significant aqueous alteration and trapped fluid inclusions. We require astromaterials that have suffered below average levels of shock, because shock often results in fluid inclusion decrepitation (loss of fluids). Thus, most aqueously-altered astromaterials we have examined have few or no remaining uncompromised fluid inclusions. We also require samples that have experienced the least terrestrial alteration, since sulfates and oxyhydroxides form rapidly in the most hydrous astromaterials, and these alterations will obscure, contaminate, modify or destroy fluid inclusions. In our experience, only asteroid Ryugu samples fit all these requirements.

We have previously obtained Ryugu samples from JAXA. Sample C0025 contains large sulfides, magnetite, magnetite and dolomite crystals and we have extracted several subsamples from C0025 using a Focused Ion Beam (FIB). We also obtained Ryugu grains A0175 and C0043, which we have begun to analyze by Micro X-ray Computed Tomography (micro XRCT). These contain abundant pyrrhotite, carbonate, apatite, and magnetite crystals with fluid inclusion candidates measuring at least 3-5  $\mu\text{m}$  in diameter, which will permit future TOF-SIMS measurements. We also have removed several pyrrhotite crystals from C0011 and A0009 via FIB for XRCT imaging.

**Micro X-ray Computed Tomography:** To determine the optimal conditions for XRCT imaging to locate suitable fluid inclusion candidates we scanned Ryugu grains at several XRCT facilities. The micro XRCT scans from the SPring-8 synchrotron facility revealed micron-sized fluid inclusion candidates in pyrrhotites and carbonates. The highest resolution micro

XRCT instrument at the University of Texas High-Resolution X-ray Computed Tomography Facility (UTCT) is the Zeiss 620 XRM, with feature detectability down to  $\sim 0.5 \mu\text{m}$ . The UTCT scans of Ryugu samples clearly resolved fluid inclusion candidates larger than  $\sim 2 \mu\text{m}$  (the minimum size for useful TOF-SIMS measurements) in crystals of pyrrhotite, carbonates, and probable apatite (Fig. 1).



**Fig. 1.** XRCT “slices” of Ryugu crystals in sample A0175, at the same scale. Fluid inclusion candidates are arrowed. (a-c) Three pyrrhotite crystals; (d,e) Two carbonate crystals; (f) A possible apatite crystal, with included magnetite spherules (white).

**Fluid Inclusion Bulk Elemental and Molecular Compositions** The TOF-SIMS analyses are performed at the University of Texas Materials Institute (TMI). We have been developing unique analytical protocols for astromaterial fluid inclusions at this facility [3]. Our pre-2023 work used an ion-TOF GmbH TOF.SIMS 5 instrument that permits sample cooling to  $-160^\circ\text{C}$ , a hard requirement for the proposed work for volatile species as we can only analyze samples in solid form.

The TMI recently installed a new, state-of-the-art ion-TOF GmbH TOF.SIMS M6 instrument that features greatly improved extraction optics and ion-transfer and detection system. The lateral resolution is improved by a factor of 5 from  $\sim 100 \text{ nm}$  (for the TOF.SIMS 5) to  $\sim 20 \text{ nm}$  (for the M6). The mass resolution is improved by a factor of  $> 3$ , from  $\sim 10,000$  to  $> 30,000$ . The M6 also has  $> 3$  times higher elemental sensitivity, permitting

useful measurements from smaller fluid inclusions (below 2  $\mu\text{m}$ , our current lower size limit), which increases the population of useful samples. The M6 permits samples to be maintained at  $-190^\circ\text{C}$ , which improves measurements of highly volatile species such as  $\text{CO}_2$ . Even though  $\text{CO}_2$  is nominally frozen at  $-160^\circ\text{C}$ , its high vapor pressure causes it to rapidly sublime in the vacuum chamber. Lowering the sample temperature to  $-190^\circ\text{C}$  also lowers the vapor pressure of the solid at the analytical temperature and thus will significantly improve analytical sensitivity to this critical species by minimizing sublimation. Another significant improvement of the M6 is its unique delayed extraction mode for high transmission permitting simultaneous high lateral and high mass resolution, something that is not possible with the TOF.SIMS 5. This feature greatly reduces uncertainties involving mass overlaps, and thus identification of species, and permits isotopic analyses. The analysis beam can be set in either the high current (HC) or burst alignment (BA) modes, depending on whether the analysis requires high mass resolution or high spatial resolution. We use the BA mode during depth profiling to clearly identify the inclusions. The exposed inclusions are then examined in both positive and negative polarity and both HC and BA modes. This ensures that the inclusions are mapped with both high mass and high spatial resolution. The total yield (in counts) of a detected secondary ion fragment by TOF-SIMS is proportional to both the concentration of its parent compound and the ionization probability of that fragment in the matrix (the material containing the parent compound).

We have begun to measure the hydrogen and oxygen isotopic composition of synthetic fluid inclusions in halite standards using the M6 in high mass resolution mode (Fig 2). The halite standards were prepared by R. Bodnar and have trapped fluids with known D/H but unknown  $^{18}\text{O}/^{16}\text{O}$ . We also analyzed NBS 28 standard quartz with a known  $^{18}\text{O}/^{16}\text{O}$  ratio. The oxygen isotopic composition of the fluids will be confirmed later using calibrations that will be developed in future sessions. With continued calibration efforts we will determine the instrumental mass fractionation for M6, but already we have learned that the hydrogen isotopes are best measured by setting the analysis gun in “Fast Imaging” High Spatial Resolution Mode, while setting the analysis gun in “Spectrometry” mode and keeping the analyzer in “All Purpose” increasing the mass resolution in “All Purpose” mode (All Purpose Resolution) is best for oxygen. The ultimate measurement errors are TBD.

We will therefore be able to measure hydrogen and oxygen isotope concentrations in individual Ryugu fluid inclusions. Although fluid inclusions in sulfides (which contain no structural oxygen) are best suited for oxygen isotope measurements, we can analytically separate counts from the oxygen secondary ion signal in the host minerals from the oxygen signal in the trapped fluids

during data reduction, as the TOF-SIMS analysis software can apply a “Region of Interest” function to separate counts from the fluid inclusion from that of the host phase. Unfortunately, we probably cannot measure  $^{17}\text{O}$  in our samples because of mass interference with  $^{16}\text{OH}$ . Fortunately, the two oxygen isotopes we can measure are sufficient to permit comparisons to be made with ongoing work on Ryugu solid mineral pairs [4,5], such as dolomite/magnetite, by other groups. This is important as the results for Ryugu samples to date are either in conflict or indicate a rather wide range of mineralizing solution temperatures, between  $\sim 25^\circ\text{C}$  [6] and  $\sim 100^\circ\text{C}$  [5]. We hypothesize that the mineralizing fluid temperatures were quite variable, and that we will see a wide range of  $\delta^{18}\text{O}$  for the fluids.

Cometary water has a significantly higher range of D/H as compared to that in hydrous (CC) asteroids. We predict that the fluids will have a very wide range of D/H, as we found in the Monahans (1998) and Zag fluid inclusions [7], indicating a similar source of water and possibly formation location to these latter samples. Based on our recent calibration measurements we will be able to obtain useful D/H ratios for all samples straightforwardly except possibly for phosphates, which contain essential hydrogen (as OH).

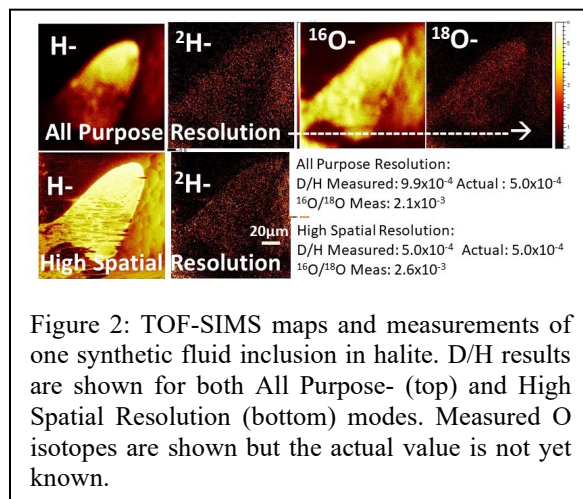


Figure 2: TOF-SIMS maps and measurements of one synthetic fluid inclusion in halite. D/H results are shown for both All Purpose- (top) and High Spatial Resolution (bottom) modes. Measured O isotopes are shown but the actual value is not yet known.

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**References:** [1] Tachibana et al. (2022) *Science* 377; [2] Nakamura et al. (2022) *Science* 377, [10.1126/science.abn8671](https://doi.org/10.1126/science.abn8671); [3] Bodnar et al. (2019) *50<sup>th</sup> LPSC Abstracts*; [4] Zheng (2011) *Geochemical Journal* 45, 341-354; [5] Yokoyama et al. (2023) *Science* 379, eabn7850; [6] Greenwood et al. (2023), *Nature Astronomy* 7, 29-38; [7] Yurimoto et al. (2014) *Reviews in Mineralogy and Geochemistry* 68, 141-186.